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# Synthesis of carbon nitride films at low temperatures

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Carbon nitride films ( $\text{CN}_x$ ) have been deposited by sputtering a graphite target with nitrogen ions. Films were grown both with and without the presence of an assisting focused  $\text{N}_2$  ion beam. The sputter beam voltage was varied between 150 and 1500 V and the applied assisting beam voltage from 80 to 500 V. The substrate was held at fixed temperatures between 80 and 673 K. The coatings were characterized with respect to their electrical, optical, and structural properties. The nitrogen content was measured by x-ray photoelectron spectroscopy (XPS) and a maximum nitrogen concentration of 44 at. % was obtained for a nonassisted sample deposited at 140 K. The chemical structure was investigated by XPS and Fourier transform infrared spectroscopy. Reduction of the substrate temperature in conjunction with low sputter beam voltages ( $<200$  V) caused the optical band gap to increase up to 2.2 eV, the sheet conductivity to decrease to less than  $10^{-9} (\Omega \text{ cm})^{-1}$  and the density to be reduced to  $1.6 \text{ g/cm}^3$ . The increasing transparency is accompanied by structural changes indicating a transition from a predominantly  $sp^2$  bonded amorphous  $sp^2/sp^3$  C–N network to a more linear polymerlike structure consisting predominantly of doubly and triply bonded C and N atoms. No evidence for the formation of the  $\beta\text{-C}_3\text{N}_4$  phase was found. © 1997 American Vacuum Society. [S0734-2101(97)02801-7]

## I. INTRODUCTION

Recently it has been found that in addition to the well known effect of physical sputtering, chemical sputtering occurs if a carbon film is bombarded with nitrogen ions.<sup>1–3</sup> Physical sputtering results in the release of neutral carbon atoms from the target. The physical sputter coefficient is a function of energy but can be almost disregarded below 100 eV. Conversely, chemical sputtering leads primarily to the formation of carbon nitride (CN) radicals. These radicals react with themselves to form  $\text{C}_2\text{N}_2$  or with superficially adsorbed water molecules to form HCN or HOCN. The estimated sputter coefficient has been shown to be about  $0.25\% \pm 20\%$  [carbon atoms/nitrogen atoms], this value being almost independent of the assisting  $\text{N}_2^+$  beam energy in the range of sputter beam voltages of 100–500 V and about a factor of 3 higher than the physical sputter coefficient for  $\text{Ar}^+$ .<sup>1</sup>

The occurrence of chemical sputtering opens up a new possibility of synthesizing carbon nitride films by dual ion beam sputtering. If contrary to conventional methods, the carbon target is bombarded with nitrogen ions, both neutral C atoms and nitrogen rich CN based compounds are sputtered. By variation of the beam energy, it is possible to influence the ratio of these (chemically) sputtered CN compounds and the (physically) sputtered C atoms. Furthermore, at deposition temperatures below the boiling point of the N rich compounds, the loss of molecules will be inhibited, increasing the N content of the film. Finally, if the growing film is bombarded by nitrogen ions, the nitrogen content

might be further increased and a rearrangement of the deposited atoms and molecules into the desired  $\beta\text{-C}_3\text{N}_4$  phase<sup>4</sup> induced by the additional energy transfer.

This article reports on carbon nitride coatings which have been synthesized with this new method. The coatings were characterized by Fourier transform infrared (FTIR), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), x-ray reflectivity, optical spectroscopy, conductivity, and hardness measurements.

## II. EXPERIMENT

The dual ion beam sputter deposition apparatus described elsewhere in detail<sup>1</sup> is equipped with two Kaufman sources of 3 cm diameter as the sputter and assisting guns. A graphite target (purity  $>99.99$  at. %) was sputtered by nitrogen ions at different voltages between 100 and 1500 V with a total ion beam current of 18–35 mA. The focused assisting nitrogen ion source was operated at voltages between 80 and 500 V with a total beam current of 1.5–8.5 mA. Focusing the ion beam graduates the intensity and hence the ion-to-atom arrival ratio at the substrate. At flow rates of 5 sccm for the sputter gun and 2 sccm for the assisting gun, the working gas pressure was maintained at  $4 \times 10^{-2}$  Pa. Sapphire and silicon wafers (100) were used as substrates. These were cleaned in an ultrasonic bath, first with a cleaning solution, then by distilled water and finally in propanol. Before deposition, the vacuum chamber was evacuated by a  $450 \text{ l s}^{-1}$  turbomolecular pump to a base pressure of  $3 \times 10^{-5}$  Pa. The substrate holder was cooled down (using liquid nitrogen) or heated up to defined temperatures of 80, 140, 230, 310, and 673 K, the temperature being monitored by a PT 100 thermocouple. Sputter cleaning of the substrates was performed using a 500 V/10 mA nitrogen ion beam.

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TABLE I. Details of the deposition parameters and measured properties of  $\text{CN}_x$  films grown at high and low sputter voltages and substrate temperatures between 80 and 673 K.

Sample	Deposition beam voltage $U_b$ (V)	Substrate temperature (K)	Optical band gap $E_{\text{tauc}}$ (eV)	Conductivity $\sigma$ ( $\Omega \text{ cm}$ ) <sup>-1</sup>	Hardness (GPa)	Nitrogen content (at. %)
CN42	1500	673	0.20	1	20	24
CN58	1000	140	0.27	1	8	
CN54	150	310	0.26	$8.7 \times 10^{-3}$	8	32
CN65	150	230	0.60	$1.0 \times 10^{-4}$	7	
CN55	150	140	1.35	$8.0 \times 10^{-10}$	1	44
CN67	150	80	2.20	$1.0 \times 10^{-14a}$	1	

<sup>a</sup>Values determined by extrapolation.

Films were analyzed *ex situ* by XPS with a Riber Nanoscan 50 incorporating a semi-imaging MAC2 analyzer. The spectra were recorded using Al  $K\alpha$  radiation at an energy resolution of 0.5 eV. The spectrometer was calibrated on the Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  peaks at 83.98 and 932.67 eV, respectively. To quantitatively examine  $\text{CN}_x$  films *ex situ* by XPS, any surface contamination must be removed with minimal artificially induced changes to the underlying bulk material. The presence of adventitious carbon contamination falsely reduces the nitrogen concentration measured at the surface and distorts the XPS C 1s peak shape.<sup>5</sup> However, sputtering induces a preferential loss of nitrogen.<sup>3,5</sup> Spectra which most faithfully reproduced the bulk material were obtained after a sputtering to a depth of approximately 6 Å. In this trade-off situation, an ion etch to a depth of approximately 6 Å was found to always remove the contamination and induce a maximum loss of 3 at. % N.<sup>5</sup> As the N concentration can only be lowered by these distortive effects, the maximum value obtained before or after the etch was taken, giving an error of up to 2 at. % in the quoted value. Curve fitting was performed with a nonlinear least-squares fitting program using a mixed Gaussian–Lorentzian product function. A Shirley background was subtracted prior to fitting. Transmission infrared (IR) spectra were measured with a Perkin Elmer FTIR 1600 spectrometer.

X-ray diffraction patterns were measured by an in-house constructed glancing angle x-ray diffractometer. The density was obtained from x-ray reflectivity measurements using a Siemens D5000 x-ray diffractometer. For all films, the surface conductivity (Keithly 617 electrometer) and Tauc band gap from UV/vis spectroscopy (Perkin Elmer 551S) have been determined. Hardness measurements were performed by an ultralow load, depth sensing nanoindenter (Nanoindenter II from Nano Instruments Inc.). The measurements were calibrated with a Si(111) wafer, assuming a modulus of 157 GPa, independent of penetration depth. With these assumptions the hardness is 12 GPa for the Si wafer, also independent of penetration depth.

### III. EXPERIMENTAL RESULTS

#### A. Band gap, conductivity, density, and hardness

Table I lists some of the films synthesized in this work, their deposition parameters, the optical band gap, dark

conductivity, hardness, and nitrogen content. As noted previously,<sup>2</sup> in the presence of an assisting  $\text{N}_2^+$  beam, the N content increases with increasing flux. However, it produced only minor changes in the band gap, dark conductivity, IR absorption, and XPS spectra.

Two  $\text{CN}_x$  films were deposited at high sputter beam voltages, one deposited at high temperature (673 K) and the other at low temperature (140 K). Both films had a dark brown color, an optical (Tauc) band gap of 0.2–0.3 eV, and dark conductivity of approximately  $1 (\Omega \text{ cm})^{-1}$ . Four films were deposited at low sputter beam voltages of 150 V. Such a decrease in the sputter beam voltage at room temperature is accompanied by a drop in the conductivity to  $9 \times 10^{-3} (\Omega \text{ cm})^{-1}$ . Progressive reduction of the substrate temperature down to 80 K produces transparent films with a Tauc gap of up to 2.2 eV and a conductivity which further decreases by 12 orders of magnitude. Assisting the growing films under these conditions with an 80–400 V  $\text{N}_2^+$  beam tended only to slightly reduce the band gap and increase the conductivity.

The effect of decreasing substrate temperature on optical band gap is displayed in Fig. 1. Both values obtained from films sputtered at a high beam voltage (open squares) are low, the reduction of the deposition temperature to 140 K producing no significant change. Conversely, the film depos-

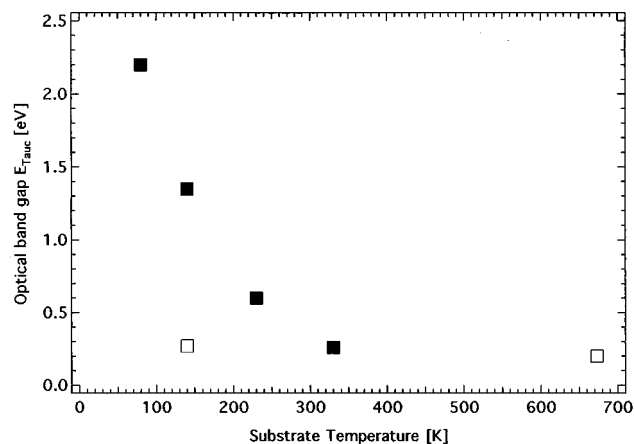


Fig. 1. Optical band gap ( $E_{\text{tauc}}$ ) vs deposition temperature for the  $\text{CN}_x$  films given in Table I (sputter beam voltages: 1000 V or above—open squares; 150 V—full squares).

ited at the same temperature, but at a low sputter voltage of 150 V (full squares) shows a considerably higher band gap of 1.35 eV. The highest Tauc gap was found for the film deposited at the lowest substrate temperature of 80 K and lowest beam voltage.

The hardness of the films depends on substrate temperature, sputter beam voltage, and nitrogen content. For the two films sputtered at high beam voltages (CN42 and CN58), there is a decrease in the hardness from 20 (673 K) to 8 GPa (140 K), whereas for the films sputtered at low beam voltages the hardness is reduced from 8 (310 K) to 1 GPa (80 K). The influence of the beam voltage (assuming similar nitrogen contents) can be seen by comparing the two films sputtered at the same substrate temperature but different beam voltages (CN58 and CN55), the hardness decreasing from 8 to 1 GPa, respectively. This decrease in hardness is accompanied by a reduction of the film density from a value of 2.2 for CN58 to 1.6 g/cm<sup>3</sup> for CN67. From substrate bending experiments, it was found that the transparent films are nearly free of internal stress and furthermore, relatively easy to scratch.

Glancing angle x-ray diffraction measurements have shown that both high and low temperature deposited films are x-ray amorphous.

## B. IR spectra

With regard to the changes in chemical structure, Fig. 2 shows the transmission IR spectra for all of the samples in Table I. In addition, the spectrum of *a*-C film sputtered with Ar<sup>+</sup> at 80 K is given. In some of the spectra, the peak at approximately 2350 cm<sup>-1</sup> is a background contribution due to the presence of traces of CO<sub>2</sub> in the measuring chamber.

The *a*-C film spectrum is featureless. Incorporation of N into the structure activates forbidden vibrational modes and absorption bands emerge in the transmission spectrum corresponding to different CN bonds. Considering first the main band, for high sputter voltages, the structure is similar with the absorption maximum occurring at 1300 cm<sup>-1</sup> for CN42 and around 1420 cm<sup>-1</sup> for CN58. As the sputter voltage is reduced to 150 V, at 310 K there is still a broad band with the maximum shifting to about 1520 cm<sup>-1</sup>, showing that the vibrational frequencies at higher wavenumbers are becoming increasingly active. Interpretation of this very broad band has best been described by Kaufmann *et al.*<sup>6</sup> These authors assigned the strong broad band with an absorption maximum at around 1570 cm<sup>-1</sup> to be indicative of large *sp*<sup>2</sup> domains, corresponding to the Raman "G" (graphitic) band. At lower wavenumbers, a broad band with the maximum at 1370 cm<sup>-1</sup> is considered to represent a more disordered structure with smaller *sp*<sup>2</sup> domains and is labeled the "D" (disordered) band. On this basis, the shift in the maximum to higher wavenumbers can be interpreted as representing an increase in the number of aromatic N-*sp*<sup>2</sup> C bonds. The contribution of the N-*sp*<sup>3</sup> C bonds, expected at lower wavenumbers, is reduced. As the deposition temperature is reduced to 140 and 80 K, there is much less absorption at lower wavenumbers, more structure, and at 80 K the maxi-

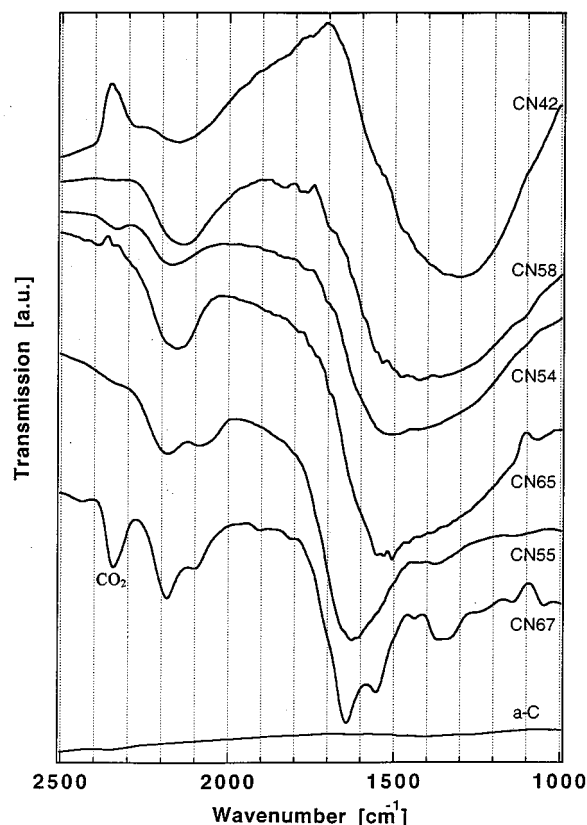


FIG. 2. FTIR transmission spectra of the CN<sub>x</sub> films given in Table I CN42 (1500 V, 673 K); CN58 (1000 V, 140 K); CN54 (150 V, 310 K); CN65 (150 V, 230 K); CN55 (150 V, 140 K); CN67 (150 V, 80 K); *a*-C film sputtered with Ar<sup>+</sup> at 80 K.

um has shifted to about 1645 cm<sup>-1</sup>. These changes represent, respectively, reduced single bonding, fewer aromatic based structures, and the presence of doubly bonded components. The exact nature of the doubly bonded groups is not determinable due to the overlap of C=C and C=N stretching vibrations in the 1600–1650 cm<sup>-1</sup> region.

For the smaller 2100–2200 cm<sup>-1</sup> absorption band, at high deposition voltages, the peak is centered at 2135 cm<sup>-1</sup>, corresponding to carbodiimide (>N=C=N<) and/or isonitrile (C≡N—) groups. This peak appears for deposited films with N concentrations above approximately 20 at. % and (for 673 K deposited films) increases in intensity with increasing N content.<sup>2</sup> For a deposition voltage of 150 V, as the temperature is reduced, the peak narrows, and two components emerge at 2100 and 2190 cm<sup>-1</sup>. These peak positions correspond to a number of different possible bonding configurations found in the literature.<sup>7,8</sup> Of particular interest are the absorption frequencies of HCN and C<sub>2</sub>N<sub>2</sub>, occurring at 2095 and 2165 cm<sup>-1</sup>, respectively. Another possible configuration found is that of a chain containing N, doubly bonded C, and terminating in a nitrile group, showing absorption at 2190 cm<sup>-1</sup>. However, exact assignment of these peaks is difficult as the peak position can be shifted by a change of environment and the double peak at 2100 and 2190 cm<sup>-1</sup> may indicate the presence of only a single group, e.g., the isonitrile group, in two different environments. These chemical groups

TABLE II. The FTIR absorption band positions for different possible bonding configurations in CN<sub>x</sub> films (taken from Refs. 7 and 8).

Absorption band [cm <sup>-1</sup> ]	Chemical group	Bonding configuration
1330–1370 “D band”	disordered $sp^2/sp^3$	$\equiv\text{C}-\text{N}<+\equiv\text{C}=\text{N}=\text{}$
1530–1570 “G band”	graphitic $sp^2/sp^3$	$=\text{C}=\text{N}=\text{}+\equiv\text{C}-\text{N}<$
1580–1680	C=N, C=C, or C=C+N in chain	$>\text{C}=\text{N}-$ , $>\text{C}=\text{C}<$ $>\text{N}-\text{C}=\text{N}-$ , $>\text{C}=\text{C}-\text{N}$
2105–2155	carbodiimide	$-\text{N}=\text{C}=\text{N}-$
2115–2175	isonitrile	$-\text{N}\equiv\text{C}$
2220–2230	nitrile	$-\text{C}\equiv\text{N}$

are clearly very similar and for convenience, this structure will be considered simply as C≡N. Some general bonding configurations found in the literature corresponding to the peaks present in these spectra are given in Table II.<sup>7,8</sup>

### C. XPS spectra

The XPS N 1s results for samples CN42, CN54, and CN55 are presented in Fig. 3. The N 1s peak fitted spectra are given as it is this data which is more informative in following the changes in chemical structure. (It should be noted that there was a charge shift of approximately 0.8 eV for the 140 K deposited sample, due to the low conductivity, which has been corrected in Fig. 3).

The N 1s peak for the 1500 V, 673 K deposited sample (CN42) is comprised of 3 components. The largest component occurs at 398.4 eV and the second component is found at 400.25 eV. The third, very small peak occurs at 402.8 eV. The peak shape for the 150 V, 310 K sample (CN54) is almost identical. A reduction in the deposition temperature for this sputter voltage of 150 V results in a very weak 400.25 eV peak. For all spectra, the splitting of these two peaks was always found to be between 1.8 and 1.9 eV. (In two of the spectra, the small peak occurring at around 395.0 eV is the Mo 3p<sub>1/2</sub> peak, present as a low concentration impurity from the molybdenum grids of the ion gun in the deposition chamber).

The assignment of the N 1s peaks are as follows. Sjöström *et al.*<sup>9</sup> have reported calculations of two model systems in which a N atom is surrounded by  $sp^2$  hybridized C (hexagonal C planes) or  $sp^3$  hybridized C atoms. A N 1s binding energy difference of 1.8 eV between the two different structures was obtained. N- $sp^3$  C bonding corresponds to the peak at 398.4 eV and N- $sp^2$  C to the peak at 400.25 eV. A depth profile of the 310 K sample, showed a slight increase of the small 402.8 eV peak with depth, indicating that this peak corresponds to a bonding configuration within the material and is not due to oxidation or surface contamination.<sup>5</sup> The origin of a peak at this high binding energy is not clear, but it is only found when the N- $sp^2$  C component is present and is probably a configuration involving planar N-N bonding.

Returning to the IR spectrum, in addition to N- $sp^2$  C and N- $sp^3$  C bonding, the high energy peaks at 2100–2200

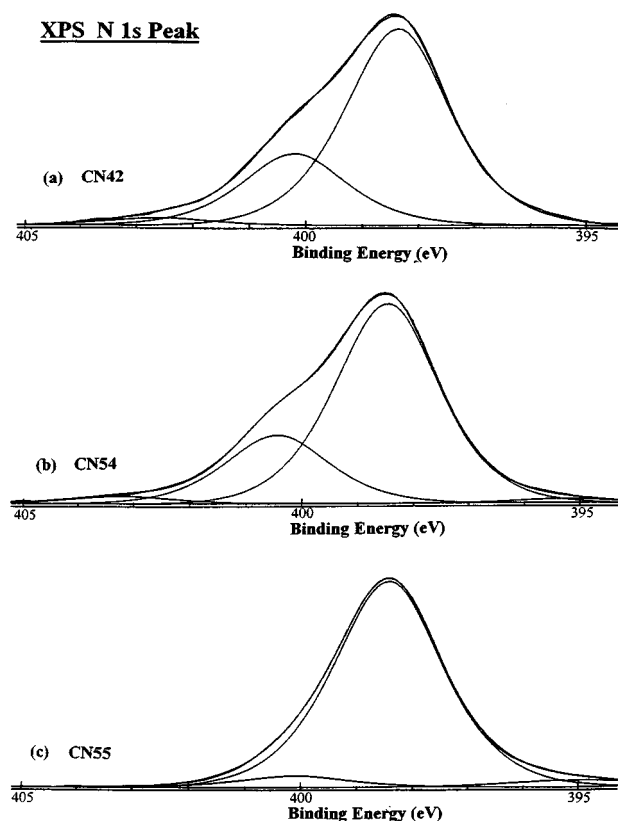


FIG. 3. XPS N 1s spectra for three of the CN<sub>x</sub> films given in Table I (a): CN42 (1500 V, 673 K) (b): CN54 (150 V, 310 K) (c): CN55 (150 V, 140 K).

cm<sup>-1</sup> correspond to C≡N configurations and the 150 V, low temperature depositions show a strong peak at 1600–1650 cm<sup>-1</sup> due to doubly bonded groups C=N and C=C.

As the CN structure changes from that based on a disordered  $sp^2/sp^3$  hybridized carbon into a double and triple bonded structure, no new components emerge in the N 1s peak. On the contrary, when the aromatic component becomes very weak, only one peak remains at 398.4 eV. This indicates that  $\equiv\text{C}-\text{N}<$  ( $sp^3$  C),  $>\text{C}=\text{N}-$  ( $sp^2$  C), and  $\text{C}\equiv\text{N}$  ( $sp$  C) type structures all exhibit the same binding energy at approximately 398.4 eV. Support for this comes from the literature, where the  $\equiv\text{C}-\text{N}<$  and  $>\text{C}=\text{N}-$  structures, have been reported to have binding energies of 398.4<sup>10,11</sup> and 398.5 eV,<sup>12</sup> respectively. The N 1s peak position for  $-\text{C}\equiv\text{N}$  (nitrile) has been given as 399.4 eV,<sup>13</sup> but the binding energy for  $-\text{N}\equiv\text{C}$  (isonitrile) would be expected at a lower value, due to the higher electron density at the N atom. The similarity of the  $-\text{N}=\text{C}=\text{N}-$  (carbodiimide) and  $>\text{C}=\text{N}-$  configurations also suggests that a binding energy of the same order is to be expected. Thus, it appears that in all aliphatic CN configurations, saturated or unsaturated, when N is bonded to more than one C atom, the distribution of the valence electron density around the N atom, and hence N 1s binding energy, is very similar.

The C 1s peaks for all of the samples are broad and rather featureless. With increasing N content, the peak broadens

and shifts to higher binding energies due to the increasing number of C–N bonds. The uncertainty of the many exact chemical environments makes a detailed interpretation and peak fitting untenable. However, for a 673 K sample with a N concentration of  $\sim 20$  at. %, the C peakshape can be well reproduced by a simulation incorporating peaks representing the possible C sites in an  $sp^2/sp^3$  amorphous C type structure.<sup>5</sup>

#### D. Coupled interpretation of IR/XPS spectra

It is now possible to make a detailed comparison of the IR and XPS results for the different samples. The high deposition voltage 673 K deposited sample (CN42), with the main IR absorption band having a maximum at around  $1300\text{ cm}^{-1}$ , indicates a mostly disordered  $sp^2/sp^3$  structure. The presence of the two N 1s peaks at 398.4 (N– $sp^3$  C) and 400.25 eV (N– $sp^2$  C) is in agreement with this. From the N 1s spectrum of the 673 K sample, the large intensity of the 398.4 eV component shows that N prefers a configuration in which it is bonded to  $sp^3$  hybridized C. The atomic percentage of N bonded to  $sp^2$  C for this sample was calculated to be 6.0%.

The film deposited at 150 V and 310 K (CN54), shows a shift in the main absorption band to higher wavenumbers—towards the G band at  $1550\text{ cm}^{-1}$ . Consequently, an increase in the N– $sp^2$  C/N– $sp^3$  C ratio would be expected in the XPS spectrum. However, in Fig. 3, the 400.25 eV/398 eV peak ratio for the 310 K sample is unchanged with respect to that for the 673 K sample. Evidence from other samples grown at beam voltages above 1000 V, has suggested this to occur as a result of a rise in the fraction of  $\text{C}\equiv\text{N}$  type bonds as the N content increases from 20 to 40 at. %, the  $\text{C}\equiv\text{N}$  overlapping with the N– $sp^3$  C component at 398.4 eV.<sup>5</sup> This behavior is in agreement with the IR spectrum for the 1000 V, 140 K grown CN58 sample, but is not so evident for the 150 V, 310 K sample. For this latter case, at a beam voltage of 150 V and substrate temperature of 310 K, a small amount of  $>\text{C}=\text{N}$ —bonding (which also overlaps the 398.4 eV component) may also be present in the structure. The 140 K sample (CN55) shows an increase in the absorption at  $1630\text{ cm}^{-1}$  and reduction in the intensity around  $1500\text{ cm}^{-1}$ . In addition, there is low intensity at low wavenumbers, indicating few singly bonded structures. In the N 1s spectrum, the aromatic component has reduced to an almost negligible value. The film structure is approaching that of an aliphatic  $\text{CN}_x$  polymer.

#### IV. DISCUSSION

Carbon nitride films deposited using a high sputter voltage at 673 and 140 K show small variation in their optical, electrical, and structural properties. At this high sputter beam and voltage, predominantly neutral carbon atoms are sputtered from the target and the chemical bonding between carbon and nitrogen to form the  $\text{CN}_x$  layer is occurring on the growing film surface. The spectral results together with the relatively high conductivity and the low band gap suggest an electronic structure having a large number of delocalized

$\pi$ -type band tail states indicating a structure based on that of  $sp^2/sp^3$  amorphous carbon. N is incorporated into both  $sp^2$  and  $sp^3$  hybridized structures, the latter being the preferential site.

Reducing the sputter beam voltage to 150 V results in a change in the sputter gas composition. In addition to neutral carbon, HCN and  $\text{C}_2\text{N}_2$  molecules are also present. At 310 K, this has little effect on the film structure and properties as these molecules are volatile at this temperature. The conductivity is slightly reduced. Although not clearly evident from the IR spectra, this is possibly due to some doubly bonded groups replacing the aromatic structures. The number of N– $sp^2$  C bonds has also increased, reducing the abundance of the highly delocalized graphitic rings.

As the substrate temperature is reduced to 140 and 80 K, the chemically sputtered molecules condense at the substrate surface causing a large change in the film properties. The band gap opens to 2.2 eV with a concomitant decrease in the conductivity. The XPS spectra show a large reduction in the amount of N incorporated into aromatic structures and the IR spectra indicate that these aromatic structures are being replaced by double bonds. As a consequence, the reduced density of delocalized  $\pi$  states increases the band gap and reduces the number of conduction electrons. There are, to a lesser extent, triple bonded and singly bonded structures. Although there is not enough data to make assertive statements, the hardness seems to decrease as (i) the beam voltage is reduced to from 1000 to 150 V, (ii) the substrate temperature is decreased, and (iii) the N content is increased above 20%.<sup>2</sup>

With respect to a growth mechanism, it can be envisaged that a deposition at low temperatures and low sputter voltages giving a structure containing a large percentage of double and triple bonds results from a limited amount of bond breaking of the triply bonded gaseous precursors of the film. When condensed at the substrate, these compounds have their surface diffusion limited by the low temperatures and hence bind together, forming a linear polymeric type structure.

As a  $\text{CN}_x$  compound which contains 44% nitrogen and is obtained by polymerization of  $\text{C}\equiv\text{N}$  containing compounds such as cyanogen and hydrogen cyanide, this film is most comparable to paracyanogen. The IR spectra given by Bircumshaw *et al.*<sup>14</sup> of paracyanogen prepared by different methods show some similarities and some differences to those obtained here. A broad band, centered at  $1570\text{ cm}^{-1}$  was observed for all samples and a peak at  $2070\text{ cm}^{-1}$  was obtained after dissolving these paracyanogens in  $\text{H}_2\text{SO}_4$  and precipitating in  $\text{H}_2\text{O}$ . The authors interpreted the results to be indicative of a complete conjugated double bond system and suggested various planar structures for the compound. It has been seen that for this film, the results support a polymeric chain and not a cyclic planar structure and that the polymer is composed of triple and single bonds in addition to the predominant double bonds.

A reduction of the sputter voltage to 150 V and substrate temperature to 140 K has enabled the nitrogen contents of  $\text{CN}_x$  films grown by dual ion beam sputtering to attain 44

at. %. A further increase of the nitrogen concentration by using high  $N_2^+$  assisting current densities is prevented by chemical etching. The polymeric structure which results from such deposition parameters, gives rise to a transparent poorly conducting film exhibiting a low density and low hardness.

## V. CONCLUSIONS

$CN_x$  films have been deposited by dual ion beam sputtering at different sputter beam voltages and substrate temperatures. At high sputter beam voltages, physical sputtering is the dominant mechanism with predominantly neutral C atoms being sputtered from the target. Films grown at substrate temperature of 673 and 140 K exhibit a similar structure and properties. These films are opaque, highly conductive, contain up to 34% nitrogen, exhibit a hardness of 20 GPa, and a density similar to that of graphite. Their structure is that of  $sp^2$  hybridized aromatic rings, cross linked by  $sp^3$  hybridized carbon, with  $C\equiv N$  groups being incorporated above a N concentration of 20%. Reducing the sputter voltage to 150 V promotes chemical etching and the sputtering of  $C\equiv N$  based molecules. At 310 K, the difference in the composition of the molecular precursors of the film have little effect on the structure and properties, the layer being similar to those produced at high sputter beam voltages. Reducing the substrate temperature to 140 and 80 K, results in only limited bond breaking of the condensing triple bonded CN species and a new  $CN_x$  phase with high nitrogen content of up to 44% is formed. This material exhibits a large optical band gap and very low conductivity. The spectroscopic in-

formation confirm that these properties occur as a result of a decrease in the delocalized aromatic component, these structures being replaced by localized double bonds. The film also contains singly and triply bonded groups. All of these groups are bound together to form a chainlike polymeric structure.

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